

# UK Patent Application (12) GB (19) 2 281 073 (13) A

(43) Date of A Publication 22.02.1995

(21) Application No 9415047.1	(51) INT CL <sup>6</sup> C08B 11/20
(22) Date of Filing 25.07.1994	(52) UK CL (Edition N ) C3A A4 A4C1 C6Y Y334 U1S S1330 S1594
(30) Priority Data (31) 9315434 (32) 26.07.1993 (33) GB	(56) Documents Cited None
(71) Applicant(s) Courtaulds Plc  (Incorporated in the United Kingdom)  50 George Street, LONDON, W1A 2BB, United Kingdom	(58) Field of Search UK CL (Edition M ) C3A A4 INT CL <sup>5</sup> C08B 11/10 11/12 11/20 Online databases: WPI, CLAIMS
(72) Inventor(s) Kevin Philip Anthony James Fowler	
(74) Agent and/or Address for Service J Y & G W Johnson Furnival House, 14-18 High Holborn, LONDON, WC1V 6DE, United Kingdom	

## (54) Hydrolysis of polysaccharides

(57) A solid mixture of a water-soluble cellulose ether generally of high molecular weight and an enzyme preparation capable of catalysing its hydrolysis can be dissolved in water under conditions of essentially simultaneous dissolution and hydrolysis of the cellulose ether to provide a solution of the cellulose ether of reduced molecular weight form. Aqueous solutions containing 15 percent or more by weight of a water-soluble cellulose ether can be prepared.

GB 2 281 073 A

HYDROLYSIS OF POLYSACCHARIDES

The present invention relates to methods of reducing the molecular weight of water-soluble polysaccharides which are cellulose ethers and to solid 5 mixtures and aqueous solutions containing cellulose ethers.

Water-soluble polysaccharides which are cellulose ethers have many uses, for example as thickeners, binders, stabilisers and flow control agents, in many industries, for example the food, pharmaceutical, cosmetic, paper and oil 10 industries. It is to be noted that the term polysaccharides includes both naturally occurring materials such as cellulose and starch and their chemical derivatives such as their ethers. Examples of water-soluble cellulose ethers include carboxymethyl cellulose, methyl cellulose, 15 hydroxyethylmethyl cellulose, ethylhydroxyethyl cellulose, hydroxyethyl cellulose and hydroxypropylmethyl cellulose.

The viscosity of a water-soluble polysaccharide, which is a measure of its degree of polymerisation (molecular weight) and chain configuration, is an important 20 technical parameter. It is generally expressed as the viscosity of a solution of the polymer at a particular concentration measured at a particular temperature under particular shear conditions. The viscosity of a water-soluble polysaccharide is a major factor in determining its 25 suitability for use in a particular application. The molecular weight and consequently the viscosity of most naturally occurring polysaccharides and their chemical derivatives is too high for many purposes. There has been increasing commercial demand over a number of years for 30 lower viscosity grades of water-soluble cellulose ethers.

Many techniques for reducing the viscosity of polysaccharides are known, including acid hydrolysis, alkaline hydrolysis, oxidation, severe mechanical treatment and enzymatic hydrolysis. The most commonly used technique

is partial hydrolysis of the polymer backbone by heating with an aqueous solution of a strong acid, for example dilute hydrochloric acid. This results in considerable loss of material by hydrolysis to small molecules such as 5 monomeric and oligomeric sugars, carbon dioxide and water. Extended or repeated treatment with acid may be necessary to obtain the lowest viscosity grades. Enzyme-catalysed solution hydrolysis is capable of providing a product which contains fewer byproducts and is less coloured with less 10 loss of material, and such hydrolysis is capable of reducing viscosity to lower levels, than can conveniently be achieved by other methods. The low-viscosity product of enzyme hydrolysis can be recovered from solution by techniques such as freeze drying and spray drying, since the major market is 15 for water-soluble polysaccharides in dry solid form. These techniques, however, require specialised equipment and are expensive to operate. It is an object of the invention to provide an improved means of providing low-viscosity water-soluble cellulose ethers.

20 R.A. Gelman in "Cellulose and its Derivatives: Chemistry, Biochemistry and Applications", edited by J.F. Kennedy (Ellis Horwood, Chichester, 1985), Chapter 25, entitled 'Characterization of Cellulose Groups: Distribution of Substituent Groups along the Chain', describes the 25 hydrolysis of carboxymethyl cellulose and hydroxyethyl cellulose catalysed by a cellulase. The starting materials had an average degree of polymerisation (D.P.) in the range 408 to 5750. Hydrolysis was conducted in aqueous solution, typically containing 0.24% by weight of the cellulose ether, 30 for 8 days at an unspecified temperature. The hydrolysed product had D.P. in the range 40 to 669, but it was not recovered from solution.

EP-A-382,577 describes the hydrolysis of a water-soluble cellulose derivative in a reaction catalysed by an 35 enzyme preparation to form a mixture of oligomers having an average D.P. in the range 3 to 300 and a molecular weight in

the range 500 to 100,000. The cellulose derivative is preferably a cellulose ether. The hydrolysis is carried out in an aqueous solution containing up to about 6% by weight of the cellulose derivative for about 24 hours at 40°C, and 5 the hydrolysed product is recovered by cooling and freeze drying or by evaporation and spray drying.

The invention provides in one aspect a method of reducing the molecular weight of a water-soluble cellulose ether by enzymatic hydrolysis, characterised in that a solid 10 mixture of (1) the cellulose ether and (2) an enzyme preparation capable of catalysing the hydrolysis of the cellulose ether is mixed with water under conditions such that essentially simultaneous dissolution and hydrolysis of the cellulose ether take place.

15 The invention also provides a method of preparing an aqueous solution of a water-soluble cellulose ether having low molecular weight, characterised in that a solid mixture of (1) a cellulose ether having high molecular weight and (2) an enzyme preparation capable of catalysing 20 the hydrolysis of the cellulose ether is mixed with water under conditions such that dissolution of the cellulose ether and its hydrolysis to low molecular weight cellulose ether take place essentially simultaneously.

The invention provides in a further aspect a solid 25 mixture which comprises (1) a water-soluble cellulose ether having high molecular weight and (2) an enzyme preparation capable of catalysing the hydrolysis of the cellulose ether to low molecular weight cellulose ether when the mixture is dissolved in water.

30 It should be understood that the terms "high molecular weight" and "low molecular weight" as used in the last two paragraphs are relative terms.

Many water-soluble cellulose ethers usable in the

invention are known, for example methyl cellulose (MC), hydroxyethylmethyl cellulose (HEMC), hydroxyethyl cellulose (HEC), ethylhydroxyethyl cellulose (EHEC), hydroxypropylmethyl cellulose (HPMC) and in particular 5 carboxymethyl cellulose (CMC). The invention is applicable to technical and to purified grades of cellulose ethers.

The molecular weight of a water-soluble cellulose ether (or other polysaccharide) is conveniently estimated and reported by measurement of the viscosity of a solution 10 of the polysaccharide in water. Water-soluble cellulose ethers are commercially available having viscosities in the range 3 to 100,000 centipoise (equal to 3 - 100,000 mPa.s) measured on a 2% by weight solution in water under low-shear conditions at ambient temperature. Water-soluble cellulose 15 ethers of high molecular weight for use in the invention preferably exhibit a 2% solution viscosity in the range 3 to 30,000 centipoise, more preferably 10 to 30,000 centipoise, further preferably 50 to 5,000 centipoise. When the solution has a viscosity below about 10 centipoise its 20 viscosity may conveniently be measured by use of an Ostwald viscometer chosen to give a flow time of more than 100 seconds when the solution has a viscosity of about 10 centipoise or less. When the solution has a viscosity above about 10 centipoise its viscosity may conveniently be 25 measured by use of a Brookfield viscometer, for example a Brookfield RVT viscometer equipped with a suitable spindle at a speed of up to about 100 rpm.

Water-soluble cellulose ethers are hydrophilic substances, and in their normal commercial air-dry form as 30 powders or granules they generally contain a small amount of water in equilibrium with the moisture in the atmosphere, for instance up to 5% or 10% by weight. Such air-dry cellulose ethers are suitable for use in the invention and are generally preferred. Bone-dry cellulose ethers may also 35 be used, but it is generally not necessary to submit to the difficulty of working under bone-dry conditions.

A variety of enzyme preparations suitable for use in the invention is available commercially. Such preparations are typically obtained from cultures of microorganisms, from which cell debris and other unwanted biological materials, including other enzymes, have been at least to some extent removed. It should be noted that the nature and activity of commercially available enzyme preparations vary quite widely, depending on the particular organism from which they are isolated and on the particular supplier. The enzyme preparation is preferably a cellulase preparation. Cellulase preparations are generally enzyme complexes, the components of which participate in the stepwise breakdown of cellulose and its derivatives. Purified cellulases containing single enzymes are also known, but they are less readily available and are generally less preferred for use in the invention than enzyme complexes. Cellulase preparations suitable for use in the invention can be obtained from microorganisms such as those of the genera Trichoderma (such as T. reesei or T. viride), 20 Aspergillus (such as A. niger), Penicillium (such as P. funiculosum), Acremonium (such as A. cellulolyticus), Cellumonas (such as C. firmi), Humicola (such as H. insolens), Clostridium (such as C. thermocellum) and various species of Fusarium, Streptomyces, Bacillus and Pseudomonas.

25 Enzyme preparations suitable for use in the invention generally have an activity in the range 100 to 10,000 units/g, preferably 500 to 5000 units/g, where the unit of enzyme activity is defined as that which releases 1 micromole of glucose per minute from a solution in water of 30 a low-viscosity cellulose ether such as CMC at pH 4.6 and 40°C.

The solid mixtures of the invention may additionally comprise one or more buffering agents to control the pH of the solution formed when the mixture is 35 dissolved in water. For example, the mixture may comprise

a water-soluble solid aliphatic organic acid such as citric acid. Enzyme activity is pH-dependent, and the solution preferably exhibits a pH at which the activity of the enzyme is high. The preferred pH depends on the particular enzyme 5 preparation used.

The solid mixtures of the invention can be prepared by simple mechanical mixing of the cellulose ether and the enzyme preparation and the optional buffering agents, for example in a Z-blade mixer or other suitable mixer.

10 The enzyme preparation may be utilised in the form of a solid or of an aqueous solution. A solution of the enzyme may be dripped or sprayed onto the solid cellulose ether, preferably as it is mechanically mixed in a mixer, to produce the solid mixture of the invention. It may be found 15 easier to achieve thorough mixing when a solution of the enzyme is used, although generally the highest uniformity of mixing is not required, and use of a solid enzyme preparation may be preferred.

20 The solid mixtures of the invention are preferably powdery or granular solids and are preferably air-dry or dry to the touch.

The solid mixtures of the invention generally contain by weight 0.01 to 1 part of enzyme preparation per 100 parts of cellulose ether.

25 The solid mixtures of the invention have good storage life, generally of the order of one year.

When a solid mixture according to the invention is dissolved in water, the enzyme catalyses the hydrolysis of the water-soluble cellulose ether, so reducing its molecular 30 weight. The hydrolysis is rapid and is generally largely complete within the normal dissolution time of the cellulose ether in commercial applications, for example around 15

minutes at ambient or slightly elevated temperature. For example, it is generally preferred that the viscosity should fall to about one fifth to one tenth or less of the original viscosity within 15 minutes or 30 minutes. It was 5 remarkable to find that a useful degree of hydrolysis could be achieved in a short time on a commercial scale.

The methods of the invention have the advantage that lump-free solution of the cellulose ether can be prepared without the use of intensive mixers. Even if some 10 lumps are present initially, it has been found that these disperse if the solution is stirred gently for a few minutes or is allowed to stand for a few hours.

Water-soluble cellulose ethers of low molecular weight produced by the invention may exhibit a 2% solution 15 viscosity in the range 1 to 10 centipoise. They may exhibit a 10% solution viscosity below 100 centipoise, for example in the range 2 to 10 centipoise. The invention is suited to the production of solutions containing 1 to 40% by weight cellulose ether of low molecular weight.

20 One use of the invention is in the pigment coating of paper. In this process, a high-solids aqueous suspension of clay and/or calcium carbonate containing binders and thickeners is coated onto paper to improve its surface properties. The highest possible solids content is aimed for 25 in order to save energy. Use of low molecular weight binders, for example cellulose ethers such as carboxymethyl cellulose, allows the use of high solids contents. Another use is in the manufacture of paper, where a water-soluble cellulose ether may be added to the papermaking stock to 30 increase the strength of the paper. Other uses include pharmaceutical tablet coating, seed coating, applications where solutions containing high proportions of polymer solids are desired, and precursors for gelling formulations.

Known low-viscosity water-soluble cellulose ethers

such as CMC can be dissolved in water to form solutions containing up to about 5 or 8 percent by weight of the cellulose ether. Known solutions containing higher amounts of cellulose ether have very high viscosities and are accordingly difficult to handle. There is a desire in some applications for solutions which contain a higher amount of the cellulose ether at an acceptable viscosity. One example of such an application is the pigment coating of paper.

The invention further provides an aqueous solution of a water-soluble cellulose ether, characterised in that it contains at least about 15 percent by weight of the cellulose ether. The concentration of the cellulose ether in the solution is specified on the basis of pure cellulose ether. The cellulose ether may be an ionic material, in particular CMC. Technical or purified grades of the cellulose ether can be used. Technical grades of CMC commonly have an activity as CMC of about 65 to 75%. The solution may contain up to about 30 percent by weight of the cellulose ether, although in practice solutions containing up to about 20 or 25 percent by weight may be easier to prepare and to handle and may consequently be preferred. Solutions which contain about 15 to about 20 percent by weight of the cellulose ether may be further preferred. A solution according to the invention, in particular a solution containing 15 to 20 percent by weight cellulose ether, may be of water-like viscosity, that is to say the viscosity of the solution at ambient temperature under low-shear conditions is below about 50 centipoise.

The aqueous solution of the invention may be prepared by dissolving the solid mixture of the invention in water. The solid mixture is preferably added to the water portionwise with stirring. In this manner, the viscosity of the aqueous solution being prepared may be maintained at an acceptably low level throughout the dissolution process.

alternatively be prepared by adding the cellulose ether to an aqueous solution of an enzyme preparation capable of catalysing the hydrolysis of the cellulose ether. Suitable enzyme preparations are described hereinabove. The 5 cellulose ether is preferably added to the water portionwise while stirring. The aqueous solution may contain a buffering agent to control pH. For example, the buffering agent may be an organic acid such as citric acid. Use of such a buffering agent may in particular be advantageous if 10 the cellulose ether is an alkaline material such as technical grade CMC. The cellulose ether is preferably added to the aqueous solution portionwise with stirring. In this manner, the viscosity of the aqueous solution being prepared may be maintained at an acceptably low level 15 throughout the dissolution process.

The cellulose ether is preferably used in granular form, in which the granular particles may for example be predominantly 100 micron to 1 mm in size. It has surprisingly been found that the aqueous solutions of the 20 invention can be prepared more rapidly from granular particles than from fine powders. Granular material can in general be added more rapidly than fine powder to the aqueous phase without the viscosity of the mixture rising above the acceptable maximum, and this permits good 25 stirring.

The aqueous solution of the invention is conveniently made by adding the cellulose ether to the aqueous phase at room temperature or at slightly elevated temperature, for example at temperatures up to 40 to 45°C. 30 It is known that the rate of a reaction catalysed by an enzyme preparation is at a maximum within a temperature range specific for that preparation. It is also known that some water-soluble cellulose ethers, for example CMC, dissolve more rapidly in water at higher temperatures, 35 whereas others, for example methyl celluloses and HPMC, are less soluble at higher temperatures. The temperature at

which the aqueous solution is made is preferably chosen so that the hydrolysis of the cellulose ether proceeds at a similar rate to the dissolution of the cellulose ether. As a result, the viscosity of the mixture is maintained below 5 the acceptable maximum, which permits good stirring.

It has been found that higher concentration aqueous solutions according to the invention can more readily be prepared by the processes described above if a cellulose ether of relatively low initial viscosity is added to the 10 aqueous phase.

Alternatively, an aqueous solution of an enzyme preparation may be added with stirring or mixing to the cellulose ether in dry form or to an aqueous slurry of the cellulose ether. Such methods are however generally less 15 preferred. It has been found that such methods produce highly viscous intermediate pastes or slurries which are difficult to mix in a satisfactory fashion and that the time required to produce the aqueous solution of the invention can be excessively long.

20 The presence of residual enzyme in the solutions of the invention is generally acceptable in the end-uses for which they are intended. The degree of hydrolysis is self-limiting, because the enzyme is incapable of hydrolysing all the backbone linkages due to the steric effects imposed by 25 the existence of the side-chain ether radicals. In contrast, naturally occurring polymers are commonly susceptible to total hydrolysis to monomers and dimers by appropriate enzyme preparations. If desired, residual enzyme can be deactivated or denatured in known ways, for example 30 by heating or by addition of a small amount of a protease.

The invention is illustrated by the following Examples, in which all parts, proportions and percentages are by weight unless otherwise specified. Viscosities above 10 centipoise were measured using a Brookfield RVT

viscometer equipped with a No. 4 spindle rotating at 100 rpm at 25°C. Viscosities below 10 centipoise were measured using an Ostwald viscometer at 25°C, chosen to give a flow time greater than 100 seconds.

5

Example 1

Technical grade carboxymethyl cellulose (CMC) available from Courtaulds plc under the Trade Mark Courlose Z608 (5% solution viscosity 3500-6000 centipoise, degree of substitution (D.S.) 0.75 minimum, activity 65%) was blended 10 with citric acid so that a solution of the blend in water exhibited a pH of about 5.0. This corresponded to a blend of approximately 1 part citric acid and 25 parts CMC.

A solid cellulase preparation (0.1 g) in powder form available from Biocatalysts Limited under the Trade 15 Mark C013P was mixed with the CMC/citric acid blend (10 g). This cellulase preparation is derived from T. reesei, has a pH optimum of 4.6, and exhibits an activity of 3000 units/g, where the unit of activity is defined as that which releases 1 micromole glucose per minute from CMC (low-viscosity type) 20 at pH 4.6 and 40°C. The powdery mixture (10 g) was added to water (90 ml) at ambient temperature with constant stirring, whereupon it dissolved. The viscosity of the solution was then measured with the following results:

	Time	Viscosity cps
25	5 min	560
	10 min	195
	15 min	145
	30 min	60
	60 min	42
	Overnight	5

Example 2

Purified CMC (99 g) available from Metsä-Serla Oy, Finland, under the Trade Mark FinFix F4 (2% solution viscosity 4 centipoise, D.S. 0.7, activity 98%) was 5 mechanically blended with the same C013P cellulase (1 g) as used in Example 1. The powdery blend (10 g) was added to water (100 ml) with constant stirring. The viscosity of the solution was measured 15 minutes after the addition and was found to be 4.7 centipoise.

10

Example 3

A dry blend of technical grade CMC in granular form (100 g; 2% solution viscosity 70-100 centipoise, D.S. 0.8, activity 65%), cellulase (1 g; as used in Example 1) and citric acid (3.2 g) was prepared. Blended material (30 g) 15 was added in 5 g portions to distilled water (70 ml) at room temperature with stirring at 15 minute intervals, whereupon it dissolved. After addition was complete, stirring was continued for a further 1 to 6 hours until the viscosity of the solution had fallen to a workable level (100 to 500 20 centipoise). The viscosity of the solution continued to fall slowly over the next few days. The solution contained 30% CMC on an as-supplied basis and 19.5% CMC on an activity (pure) basis.

Example 4

25 Cellulase (0.29 g; as used in Example 1) and citric acid (0.92 g) were dissolved in water (70 ml). CMC (30 g; as used in Example 3) was added in 5 g portions at 15-minute intervals to the stirred solution, whereupon it dissolved. The viscosity of the solution remained 30 sufficiently low throughout the procedure for easy stirring throughout the period of addition. The viscosity of the solution decreased to a workable level over 1 to 6 hours and thereafter fell more slowly over the next few days. The

solution contained 30% CMC on an as-supplied basis and 19.5% CMC on an activity (pure) basis.

Example 5

15 A dry blend of purified CMC in granular form (100 g; 5 g; 2% solution viscosity 75 centipoise, D.S. 0.7) and cellulase (1 g; as used in Example 1) was prepared. The blended material (15 g) was added in 5 g portions at 15-minute intervals to distilled water (85 ml) at room temperature with stirring, whereupon it dissolved. Stirring 10 was continued after the addition was complete. The viscosity of the solution decreased to a workable level within 1 to 2 hours and fell to a water-like level overnight. The solution contained 15% CMC.

Example 6

15 A dry blend of purified CMC in powder form (100 g; 2% solution viscosity 450 centipoise, D.S. 0.7) and cellulase (1 g; as used in Example 1) was prepared. The blended material (15 g) was added in 1-2 g portions at 20 intervals of 10-15 minutes to distilled water (85 ml) at room temperature with stirring, whereupon it dissolved. The addition rate was necessarily slower than in Example 5 in order to maintain the viscosity of the solution below the acceptable maximum while the hydrolysis proceeded. Stirring 25 was continued after the addition was complete. The viscosity of the solution eventually fell to a water-like level. The solution contained 15% CMC.

CLAIMS

1. A method of reducing the molecular weight of a water-soluble cellulose ether by enzymatic hydrolysis, characterised in that a solid mixture of (1) the cellulose ether and (2) an enzyme preparation capable of catalysing the hydrolysis of the cellulose ether is mixed with water under conditions such that essentially simultaneous dissolution and hydrolysis of the cellulose ether take place.

10 2. A method of preparing an aqueous solution of a water-soluble cellulose ether having low molecular weight, characterised in that a solid mixture of (1) a cellulose ether having high molecular weight and (2) an enzyme preparation capable of catalysing the hydrolysis of the cellulose ether is mixed with water under conditions such that dissolution of the cellulose ether and its hydrolysis to low molecular weight cellulose ether take place essentially simultaneously .

3. A method according to claim 1 or claim 2, wherein the molecular weight of the cellulose ether in the solid mixture is such that the viscosity of a 2 percent by weight aqueous solution of the cellulose ether measured at ambient temperature under low-shear conditions is in the range 10 to 30,000 centipoise.

25 4. A method according to claim 3, wherein the said viscosity is in the range 50 to 5,000 centipoise.

5. A method according to any one of the preceding claims, wherein the molecular weight of the cellulose ether after dissolution and hydrolysis is such that the viscosity of a 2 percent by weight aqueous solution of the cellulose ether measured at ambient temperature under low- shear conditions is in the range 1 to 10 centipoise.

6. A method according to any one of claims 1 to 4, wherein the molecular weight of the cellulose ether after dissolution and hydrolysis is such that the viscosity of a 10 percent by weight aqueous solution of the cellulose ether measured at ambient temperature under low-shear conditions is in the range 2 to 10 centipoise.

7. A method according to any one of the preceding claims, wherein the cellulose ether is carboxymethyl cellulose.

10 8. A method of obtaining lower molecular weight water-soluble cellulose ether in aqueous solution by enzymatic hydrolysis carried out substantially as hereinbefore described or exemplified.

15 9. A solid mixture which comprises (1) a water-soluble cellulose ether having high molecular weight and (2) an enzyme preparation capable of catalysing the hydrolysis of the cellulose ether to low molecular weight when the mixture is dissolved in water.

10. A solid mixture according to claim 9, wherein the 20 molecular weight of the cellulose ether is such that the viscosity of a 2 percent by weight aqueous solution of the cellulose ether measured at ambient temperature under low shear conditions is in the range 10 to 30,000 centipoise.

11. A solid mixture according to claim 10, wherein the 25 said viscosity is in the range 50 to 5,000 centipoise.

12. A solid mixture according to any one of claims 9 to 11, which additionally comprises a buffering agent to control the pH of the solution formed when the mixture is dissolved in water.

30 13. A solid mixture according to claim 12, wherein the buffering agent is a water-soluble solid aliphatic organic

acid.

14. A solid mixture according to any of claims 9 to 13, wherein the cellulose ether is carboxymethyl cellulose.

15. A solid mixture of water-soluble cellulose ether 5 and enzyme preparation substantially as hereinbefore described or exemplified.

16. An aqueous solution of a water-soluble cellulose ether, characterised in that it contains at least about 15 percent by weight of the cellulose ether.

10 17. An aqueous solution according to claim 16, which contains about 15 to about 30 percent by weight of the cellulose ether.

18. An aqueous solution according to claim 17, which contains about 15 to about 20 percent by weight of the 15 cellulose ether.

19. An aqueous solution according to claim 18, wherein the viscosity of the solution measured at ambient temperature under low-shear conditions is below about 50 centipoise.

20 20. An aqueous solution according to any one of claims 16 to 19, wherein the cellulose ether is carboxymethyl cellulose.

21. A concentrated aqueous solution of a water-soluble cellulose ether substantially as hereinbefore described or 25 exemplified.

Relevant Technical Fields

(i) UK Cl (Ed.M) C3A: A4  
(ii) Int Cl (Ed.5) C08B 11/10, 11/12; 11/20

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: WPI, CLAIMS

Search Examiner  
A KERRY

Date of completion of Search  
15 NOVEMBER 1994

Documents considered relevant  
following a search in respect of  
Claims :-  
1-15

Categories of documents

X: Document indicating lack of novelty or of inventive step. P: Document published on or after the declared priority date but before the filing date of the present application.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

A: Document indicating technological background and/or state of the art. &: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).